

CHEMICAL REGENERATION OF Fe(II)-EDTA IN WET SCRUBBERS

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Key Words: Fe(II)-EDTA, chemical reduction, NO_x removal

INTRODUCTION:

Transition metal chelates have attracted the attention of researchers for the past two decades primarily because of the effectiveness of Fe(II)-EDTA in removing nitric oxide (NO) from the flue gas and its likely compatibility with wet scrubbers. However, Fe(II)-EDTA tends to get oxidized in the scrubbers and Fe(III)-EDTA is not reactive for NO removals. Several reducing agents have been proposed. The purpose of this paper is to evaluate these reducing agents including sulfite or bisulfite, the most logical ones in wet scrubbers.

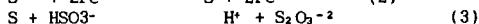
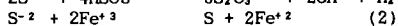
EXPERIMENTS:

Jacketed reactors were used to conduct experiments at desired temperatures. 1, 10-phenanthroline method was used to determine ferrous ions (Walker and Perry, 1989). Total iron was measured by atomic absorption. Ethylene diamine tetraacetic acid (10% excess), ferrous ammonium sulfate, and ferric ammonium sulfate were used to prepare Fe-EDTA. Sodium carbonate powder and dilute sulfuric acid were used to adjust pH.

RESULTS AND DISCUSSIONS:

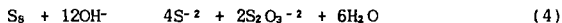
Several reducing agents were tested in batch reactors for Fe(II)-EDTA regeneration. Table 1 lists the related redox potentials. As indicated by the redox potentials, several common metals such as Fe, Zn and Al, are expected to be able to reduce Fe(III)-EDTA to Fe(II)-EDTA. Iron powder, aluminum powder and zinc dust were used to reduce 10 mM Fe(III)-EDTA. The results are summarized in Figure 1. Iron was capable of reducing Fe(III)-EDTA to Fe(II)-EDTA, which was tested and abandoned because of its poor utilization and ferric hydroxide precipitation problem (Staub, 1988). Compared to zinc or alumina, the reducing rate of Fe(III)-EDTA by iron powder was substantially lower probably due to the adverse effect of the magnetic stirring bar on iron powder distribution. Alumina was not reactive at pH 5.5. However, when the pH was raised to 9.0 its reactivity towards Fe(III)-EDTA reduction was substantially higher. Obviously, the higher pH helped dissolve the inert Al₂O₃ film on the surface of alumina. Zinc is much more effective in reducing Fe(III)-EDTA primarily because of the unit surface area of the zinc we used was substantially higher than those of iron and alumina. Although zinc and alumina are effective and efficient in reducing Fe(III)-EDTA to Fe(II)-EDTA, they are probably not adequate for Fe(II)-EDTA regeneration because the stability constants of Zn-EDTA and Al-EDTA are larger than that of Fe(II)-EDTA. If Zn-EDTA and Al-EDTA are reactive towards NO removal, they should be used in the first place because Zn-EDTA and Al-EDTA cannot be oxidized.

Hydrogen sulfide has been proposed to reduce Fe(III)-EDTA to Fe(II)-EDTA. This approach was not generally accepted because of the toxicity and the odor problem of H₂S. However, H₂S can be converted to CaS or Na₂S quite easily by reacting with Ca(OH)₂ and NaOH respectively. There are two possible reactions in scrubbing liquor when sulfide is added.



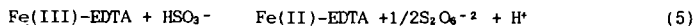
Sulfite/bisulfite competes with ferric for sulfide. The results indicated that 5 mM sulfide converted 6 mM Fe(III)-EDTA to Fe(II)-EDTA instantaneously with or without the presence of 0.1 M sulfite. In other words, the utilization of sulfide in reducing Fe(III)-EDTA was around 60%. There might be some unidentified reactions that reduce the utilization of sulfide as a reducing agent for Fe(II)-EDTA regeneration. As indicated by equations 1-3, thiosulfate will be accumulated when sulfide is used to reduce Fe(III)-EDTA. Thiosulfate was recognized as an effective free radical scavenger and was applied to wet FGD to inhibit sulfite oxidation successfully (Owens and Rochelle, 1985). Still, the effect of accumulated thiosulfate on the performance of wet scrubbers needs further study.

Theoretically, alkaline hydrolysis of sulfur (Lee et al., 1990)



can achieve a 50% conversion to sulfide as indicated by reaction 4. When the reaction is not complete, a polysulfide mixture instead of sulfide is the product. To investigate the possibility of using the sulfide/polysulfide product as the reducing agent for Fe(II)-EDTA regeneration, sodium tetrasulfide (Na₂S₄) was used to reduce Fe(III)-EDTA. The results indicated that the sulfide sulfur of the tetrasulfide was as good as sulfide in terms of reducing Fe(III)-EDTA to Fe(II)-EDTA. Unsurprisingly, the elemental sulfur of tetrasulfide did nothing except react with sulfite/bisulfite to form thiosulfate. Because alkaline hydrolysis of sulfur (reaction 4) is an inexpensive source of reducing agent, effects of accumulated thiosulfate on the performance of scrubbers deserve further investigation.

Obviously, the most ideal reducing agent for Fe(II)-EDTA regeneration in wet scrubbing system is sulfite/bisulfite. Unfortunately, the reaction rate at scrubber operating temperature (~50°C) is too slow to be practical. It is well known that the rate can be accelerated by raising the temperature, however, the effects of pH on the kinetics were reported inconsistently. Sada et al. (1984) judged that Fe(III)-EDTA reduction by sulfite/bisulfite should be enhanced by raising pH probably based on Le Chatelier principle and the following reaction.



Sada et al. (1988) reported later that reaction 5 was first order in both Fe(III)-EDTA and HSO₃⁻. In other words, Fe(III)-EDTA reduction by sulfite/bisulfite was supposed to be favored by lowering the pH of the

solution. It is contradictory to our result (Figure 2); and our result is consistent with data of Walker et al. (1988). Furthermore, Weisweiler et al. (1986) showed that NO removal was enhanced by raising pH in an ejector type 16-liter gas-liquid contactor. The mechanism is not clear yet, but our preliminary data (not shown) indicated that both Fe(II)-EDTA and dithionate suppressed the forward reaction of reaction 5. Furthermore the pH may significantly affect the activity of Fe(II)-EDTA and the stability of dithionate.

Since the regeneration of Fe(II)-EDTA by sulfite/bisulfite is not good enough to maintain high NO_x removal, the search for efficient and affordable additives or other reducing agents has been in progress. Sodium thiosulfate was tested. It itself did not show any capability for Fe(II)-EDTA regeneration. However, in the presence of sulfite/bisulfite (0.05 M S(IV)), at pH 7, 10 mM thiosulfate tripled the initial rate of Fe(II)-EDTA (10 mM) reduction. However, a couple hours later, the cumulative conversion of ferric to ferrous EDTA was not affected by the addition of thiosulfate.

Several organic "reducing agents" were also tested for the reduction of Fe(III)-EDTA to Fe(II)-EDTA. Most of these organic compounds were not satisfactory. For example, methanol can be oxidized to formaldehyde, which can then be oxidized to formic acid, and then decomposed to carbon dioxide. Based on standard redox potentials, one would predict that Fe(III)-EDTA could be reduced to Fe(II)-EDTA by each oxidation reaction mentioned above. Unfortunately, neither methanol, formaldehyde or formic acid showed any reducing capability. Both tartaric acid and maleic acid are apt to be oxidized in the air. Oxalic acid, when decomposed to carbon dioxide, was predicted to be able to reduce Fe(III)-EDTA. Unfortunately, none of these three organic acids gave positive results. However, some of the aforementioned organic compounds may act as antioxidants which will prolong the lifetime of Fe(II)-EDTA by sacrificing themselves. Maleic acid is of particular interest because it is available as waste products and it was reported to be easily oxidized under FGD conditions (Lee, 1986).

One of the most interesting organic reducing agents we studied so far is ascorbic acid or vitamin C. It was reported to be a good reducing agent for Fe(II)-EDTA regeneration, in the presence of dithionite (Holter et al., 1987). We found that ascorbic acid was a very good reducing agent even in the absence of dithionite. Furthermore, 1 molecule of ascorbic acid can reduce 10 molecule of Fe(III)-EDTA in a couple hours (figure 3). Also tested was the D-form or the optical isomer of ascorbic acid. The D-isomer demonstrated similar effect on Fe(III)-EDTA reduction as one would expect. In other words, the racemic mixture, which should be substantially cheaper than vitamin C, would be as good as L-ascorbic acid in terms of Fe(II)-EDTA regeneration. The mechanism and the products of this reaction are not clear to the authors yet.

ACKNOWLEDGMENT

The Authors would like to thank Mr. Jeff Henk, Ms. Pat Kerr and Mr. Jerry Hoffman for their help in performing the experiments, typing the paper and preparing the figures, respectively.

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TABLE 1
RELATED STANDARD REDUCTION POTENTIALS FOR Fe(II)-EDTA REGENERATION

Reduction Reaction	E _o
Fe(III)-(Phenanthroline) ₃ ³⁺ + e ⁻ → Fe(II)-(Ph) ₃ ²⁺	1.14
Fe ³⁺ + e ⁻ → Fe ²⁺	0.77
S ₂ O ₆ ²⁻ + 4H ⁺ + 2e ⁻ → 2H ₂ SO ₄	0.6
S ₄ O ₆ ²⁻ + e ⁻ → 2S ₂ O ₃ ²⁻	0.09
Fe(III)-EDTA ⁻ + e ⁻ → Fe(II)-EDTA ²⁻	-0.177*
2SO ₄ ²⁻ + 4H ⁺ + 2e ⁻ → S ₂ O ₆ ²⁻ + 2H ₂ O	-0.2
CO ₂ + 2H ⁺ + 2e ⁻ → HCOOH	-0.2
Fe ³⁺ + 2e ⁻ → Fe	-0.409
S + H ₂ O + 2e ⁻ → HS ⁻ + OH ⁻	-0.478
2CO ₂ + 2H ⁺ + 2e ⁻ → H ₂ C ₂ O ₄	-0.49
S + 2e ⁻ → S ²⁻	-0.508
2SO ₃ ²⁻ + 3H ₂ O + 4e ⁻ → S ₂ O ₃ ²⁻ + 6OH ⁻	-0.58
Zn ²⁺ + 2e ⁻ → Zn	-0.76
SO ₄ ²⁻ + H ₂ O + 2e ⁻ → SO ₃ ²⁻ + 2OH ⁻	-0.92
2SO ₃ ²⁻ + 2H ₂ O + 2e ⁻ → S ₂ O ₄ ²⁻ + 4OH ⁻	-1.12
Al ³⁺ + 3e ⁻ → Al(0.1F NaOH)	-1.706
H ₂ AlO ₃ ⁻ + H ₂ O + 3e ⁻ → Al + 4OH ⁻	-2.35

Sources

CRC Handbook of Chemistry and Physics 53rd Ed. (1972-1973)

*W. R. Grace Technical Information

Figure 1 Fe(II)-EDTA Regeneration
by Al, Zn, and Fe Powdered Metals

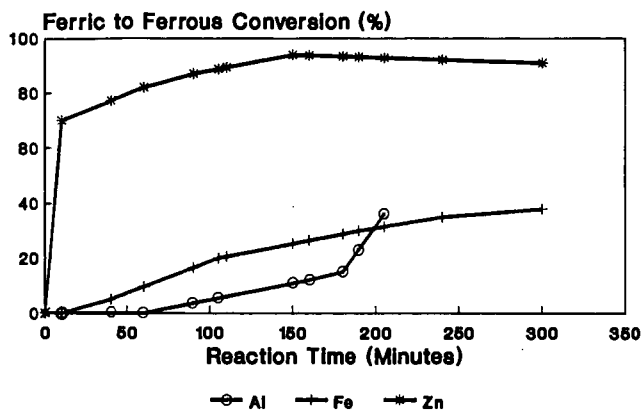


Figure 2 pH and Temperature Effects
on Fe(II)-EDTA Regeneration by Sulfite

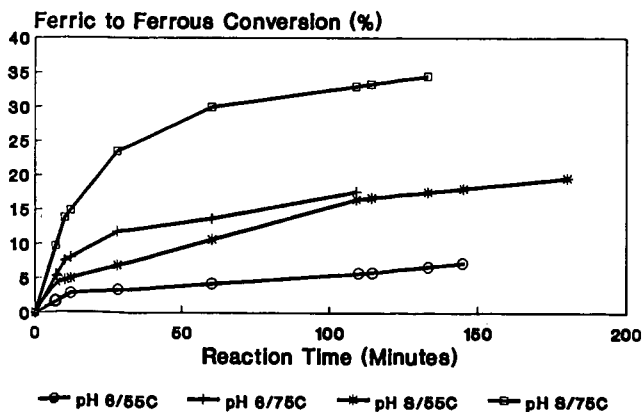


Figure 3 Fe(III)-EDTA Reduction
by L-Ascorbic Acid (Vitamin C)

